

## Photoinitiated Doping of Polyacetylene

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**Summary** Ultraviolet irradiation of polyacetylene films treated with diaryliodonium or triarylsulphonium salts leads to doping of the exposed areas and provides greater control of the doping process than can be achieved by conventional doping methods.

POLYACETYLENE,  $(CH)_x$ , has attracted considerable attention over the past three years because of its unique electronic properties. Although  $(CH)_x$  is intrinsically a wide band-gap semiconductor, its conductivity can be systematically varied over twelve orders of magnitude from  $10^{-9}$  to  $10^3 \Omega^{-1} \text{cm}^{-1}$  by treatment with a variety of oxidizing or reducing agents.<sup>1</sup> An important prerequisite to the use of polyacetylene in device-type applications, however, is the ability to dope specific areas of a film selectively in order to

generate conducting or semiconducting patterns. Simple dopant diffusion techniques using conventional masks are not applicable owing to the highly porous nature of these films.<sup>2</sup> Attempts to dope  $(CH)_x$  by ion implantation have produced mixed results.<sup>3</sup> We report here a solution to this problem using as dopants triarylsulphonium or diaryliodonium salts, species which are normally inert towards polyacetylene, but which on irradiation undergo photochemical reaction leading to doping of the polymer.

The search for materials whose photoproducts are effective dopants was aided by the discovery by Gau *et al.* that proton acids are capable of doping  $(CH)_x$ .<sup>4</sup> Crivello and Lam had previously shown that triarylsulphonium and diaryliodonium salts decompose on u.v. irradiation to produce the corresponding proton acids.<sup>5,6</sup> We now find

that the conductivities of  $(\text{CH})_x$  films impregnated with, for example, triphenylsulphonium hexafluoroarsenate can be raised to *ca.*  $2 \Omega^{-1} \text{cm}^{-1}$  on exposure to u.v. radiation, presumably as a result of proton doping. Diphenyliodonium hexafluoroarsenate proves equally effective. Irradiation of pristine  $(\text{CH})_x$  under identical conditions produces no change in conductivity or composition. (All irradiations were carried out under argon in a Rayonet reactor at 254 nm. Conductivities were measured by the four-point probe method using either pressed contacts or gold leads evaporated on to the film before treatment with the salt.)

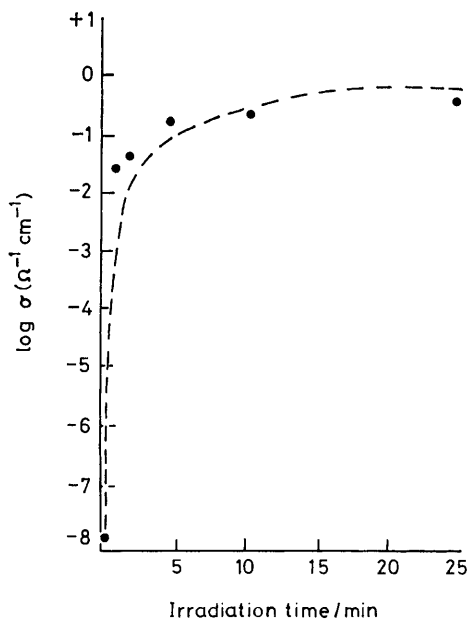


FIGURE 1. Conductivity as a function of irradiation time for  $(\text{CH})_x$  film treated with a 1 molar solution of triphenylsulphonium hexafluoroarsenate in methylene dichloride.

Since polyacetylene itself has some absorption at 254 nm, the penetration of light into the film and the resulting doping process should be a function of both film thickness and irradiation time. Figure 1 shows the conductivity of a  $50 \mu\text{m}$  thick film as a function of exposure time (both sides irradiated). The conductivity levels off after *ca.* 20 min; further irradiation produces no additional change in conductivity. To confirm that this plateau corresponds to complete reaction throughout the bulk of the film, a different sample was covered on one side and irradiated from the other. Four-point probe measurements at successive time intervals showed that, as expected, the

apparent conductivity on the covered side was considerably lower than that of the exposed side in the early stages of irradiation, but that after *ca.* 40 min both sides showed essentially equal conductivities. As hoped, masking given areas of the film from the incident radiation leads to doping only in the exposed areas. Unchanged salt in the undoped areas can be subsequently removed by washing with methylene dichloride.

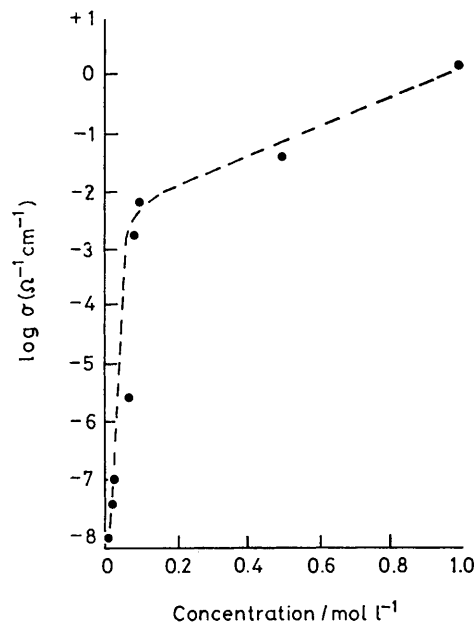


FIGURE 2. Conductivity after 20 min irradiation for  $(\text{CH})_x$  films treated with various concentrations of triphenylsulphonium hexafluoroarsenate in methylene dichloride.

Perhaps the most valuable aspect of this technique is the control which it affords over the final doping level, particularly in the low-doping regime where reproducible results are rather difficult to obtain with the conventional gas-phase dopants. Figure 2 shows the results obtained by simply dipping the  $(\text{CH})_x$  films into methylene dichloride solutions containing various concentrations of triphenylsulphonium hexafluoroarsenate, drying, and then irradiating to completion. As expected, the final conductivity scales quite reproducibly with the initial solution concentration.

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<sup>1</sup> For reviews see A. G. MacDiarmid and A. J. Heeger, *Synth. Metals*, 1979, **1**, 101; G. B. Street and T. C. Clarke, *Adv. Chem. Ser.*, 1980, **186**, 177.

<sup>2</sup> T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 11.

<sup>3</sup> W. N. Allen, P. Brant, A. Carosella, J. J. DeCorpo, C. T. Ewing, F. E. Saalfeld, and D. C. Weber, *Synth. Metals*, 1980, **1**, 151.

<sup>4</sup> S. C. Gau, J. Millikan, A. Pron, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1979, 662.

<sup>5</sup> J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 977.

<sup>6</sup> J. V. Crivello and J. H. W. Lam, *Macromolecules*, 1977, **10**, 1307.